



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01D 53/14	A1	(11) International Publication Number: WO 00/66249 (43) International Publication Date: 9 November 2000 (09.11.00)
(21) International Application Number: PCT/US00/11635 (22) International Filing Date: 1 May 2000 (01.05.00) (30) Priority Data: 09/304,283 3 May 1999 (03.05.99) US (71) Applicant: UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US). (72) Inventors: SCHUBERT, Craig, Norman; 50 Riverview Terrace, Belle Mead, NJ 08502 (US). FORTE, Paulino; 82 Homecrest Oval, Yonkers, NY 10703 (US). DEAN, John, Wayne; 34 Union Road, Clinton, NJ 08809 (US). (74) Agent: PACCIONE, Stanley, J.; Union Carbide Chemicals & Plastics Technology Corporation, 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: ABSORBENT COMPOSITIONS FOR THE REMOVAL OF ACID GASES FROM THE GAS STREAMS (57) Abstract <p>An improved absorbent composition for the removal of acid gases, such as CO₂, H₂S and COS, from gas streams is provided. The absorbent composition comprises an aqueous solution comprising: 1) greater than 1 mole piperazine per liter of aqueous solution; and 2) about 1.5 to about 6 moles methyldiethanolamine per liter of aqueous solution.</p> <p style="text-align: right;">BEST AVAILABLE COPY</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

BEST AVAILABLE COPY

ABSORBENT COMPOSITIONS FOR THE REMOVAL OF ACID GASES FROM THE GAS STREAMS

The present invention relates to an improved absorbent composition comprising an aqueous solution of piperazine and methyldiethanolamine for the removal of acid gases, such as CO₂, H₂S and COS, from gas streams.

Background of the Invention

Gas streams from natural gas wells, refineries and the like typically contain undesirable acid gases such as CO₂, H₂S, COS, and mercaptans. Aqueous amine solutions are known to be useful for the absorption of acid gases from these types of gas streams. Typically an acid gas-rich gas stream is contacted with an aqueous absorbent composition comprising an amine solution at low temperature or high pressure in an absorber. The aqueous amine solution usually contains an alkanolamine such as triethanolamine (TEA), methyldiethanolamine (MDEA), diethanolamine (DEA), monoethanolamine (MEA), diisopropanolamine (DIPA) or hydroxyaminoethyl ether (DGA). Once the acid gases are removed from the gas stream, it is ready for sale or additional downstream conditioning. The acid gas rich solution is regenerated for reuse by driving off the absorbed gases in specialized equipment such as flash tanks and/or stripper columns typically operated at high temperature or low pressure.

Workers in the art have found that certain compounds, such as piperazine and monomethylethanolamine (MMEA) may be advantageously added to aqueous amine solutions to enhance their absorption capabilities. For example, U.S. Patent No. 4,336,233 to

Appl et al. discloses a process for removing CO₂, H₂S and in some cases COS from gases that contain these compounds by washing the gases with aqueous solutions containing MDEA and piperazine as an absorption accelerator. The amount of piperazine stated to be useful in these absorbent compositions is up to 0.8 moles per liter of aqueous solution. The '233 patent also discloses that it is particularly preferred to add from 0.05 to 0.4, especially from 0.2 to 0.4, moles piperazine per liter of aqueous solution.

U.S. Patent No. 4,997,630 to Wagner et al. discloses a staged process for the removal of CO₂ and/or H₂S using an aqueous absorption liquid containing MDEA. The aqueous absorption liquid may additionally contain from 0.05 to 1, preferably 0.1 to 0.8, mole per liter piperazine.

In contrast with the teachings of the prior art, applicants have discovered that improved absorbent compositions for the removal of acid gases from gas streams instead comprise aqueous MDEA/piperazine solutions containing greater than 1 mole piperazine per liter of aqueous solution. In particular, aqueous solutions containing greater than 1 mole piperazine per liter of aqueous solution and about 1.5 to about 6 moles MDEA per liter of aqueous solution have been found to provide superior absorption capabilities over aqueous MDEA/piperazine solutions containing 1 mole or less piperazine per liter of aqueous solution. The present MDEA/piperazine absorbent compositions advantageously provide equivalent CO₂ removal at reduced absorbent composition circulation rates in the absorber and increased absorber temperature, as well as improved performance of downstream regeneration equipment.

Summary of the Invention

The invention provides an absorbent composition for the removal of acid gases from gas streams, comprising an aqueous solution comprising: 1) greater than 1 mole piperazine per liter of aqueous solution; and 2) about 1.5 to about 6 mole methyldiethanolamine per liter of aqueous solution.

The invention further provides a process for the removal of acid gases from a gas stream. A gas stream containing an acid gas contacts the above absorbent composition to produce a sweet gas stream and an acid gas-rich absorbent composition stream.

Brief Description of the Drawing

The Figure illustrates a process flow diagram of an absorption process according to the present invention.

Detailed Description of the Invention

The absorbent composition comprises an aqueous solution of piperazine and MDEA. The amount of piperazine in the aqueous solution is critical to the invention, and must be greater than 1 mole piperazine per liter of aqueous solution. Preferably, the amount of piperazine is greater than about 1.1 mole piperazine per liter of aqueous solution, and more preferably is greater than about 1.2 mole piperazine per liter of aqueous solution.

The amount of MDEA in the aqueous solution ranges from about 1.5 to about 6 moles MDEA per liter of aqueous solution. Preferably, the amount of MDEA ranges from about 2.5 to about 5.5 moles MDEA per liter of aqueous solution, more preferably from about 2.9 to about 4.2 moles MDEA per liter of aqueous solution.

The balance of the absorbent composition may be water, or the absorbent composition may optionally also comprise one or

more other chemical solvents or physical solvents. For example, amines, such as ethyldiethanolamine, methylethanolpropanolamine, ethylethanolpropanolamine, methyldipropanolamine, triethanolamine, diethanolamine, monoethanolamine, hydroxyaminoethyl ether or diisopropanolamine may be used as additional chemical solvents.

~~Physical solvents such as sulfolane or methoxytriglycol may also be~~
employed. When such chemical or physical solvents are used, they preferably make up from about 5 to about 50 weight percent of the absorbent composition, more preferably from about 10 to about 40 weight percent of the absorbent composition.

The absorption composition may also contain additives such as corrosion inhibitors, defoamers, and the like. Typically, the concentration of such additives ranges from about 0.01 to 5 weight percent based on the weight of the absorbent composition on an anhydrous basis. The use of such additives is well known to those skilled in the art.

Any gas containing an acid gas can be treated according to the present invention. The sources of such gases are not critical to the invention and include, for example, natural gas wells, synthesis gas streams and refinery gas, including refinery coker off-gas, refinery fluid catalytic cracker off-gas, refinery hydrogen units, and other refinery gas streams. Typically, these gas streams contain one or more of the following acid gases: mercaptans, CO₂, H₂S, and COS. It is also not uncommon for these gas streams to contain one or more of the following: SO₂, SO₃, CS₂, HCN and oxygen.

Mercaptans are often present in amounts ranging from about 10 to 10,000 ppmv. Up to about 90 mole percent of H₂S may be present as well. CO₂ is typically present in amounts ranging up to about 50

mole percent, often from about 1 to 15 mole percent. COS, when present, typically comprises from about 2 to 10,000 ppmv. The remainder of such gases is usually hydrocarbons, hydrogen, carbon monoxide, nitrogen and other light gases.

Gas streams containing acid gases are treated to remove the acid gases by contacting with the absorbent composition of the invention. Preferably, the used absorbent composition, that is, the

acid gas-rich absorbent composition, is regenerated to remove all or part of the absorbed acid gases, and then recycled to the absorption step. Any equipment known in the art may be used for absorption, regeneration, and the rest of the process.

The Figure is a flow diagram of a typical process for the removal of acid gases in accordance with the invention. A feed gas stream containing acid gases is introduced to absorption zone 100 via line 10. Absorption zone 100 comprises a gas-liquid contacting tower containing suitable trays or packing material to conduct absorption. Details concerning the apparatus used in the absorption zone are known to those skilled in the art. The absorption zone is typically operated at a temperature of about 25 to 90° C and a pressure of about 15 to 1500 psia.

In absorption zone 100, the feed gas stream introduced via line 10 is contacted with the absorbent composition stream introduced via line 11. A product gas stream that is depleted in the acid gases relative to the feed gas stream is discharged from absorption zone 100 via line 12. Preferably, at least about 50 percent of the acid gases are removed from the feed gas stream in absorption zone 100. An acid gas-rich absorbent composition stream is withdrawn from absorption zone 100 via line 13.

The acid gas-rich absorbent composition may pass through one or more flash zones. The Figure shows one such zone (300). A fraction

of the absorbed gases is separated from the acid gas-rich absorbent composition and emerges in line 19. The balance of the material in line 13 emerges from flash zone 300 via line 14.

The acid gas-rich absorbent composition stream is introduced via line 15 to a regeneration zone 200 wherein remaining acid gases are desorbed from the absorbent composition. Regeneration zone 200 often comprises a distillation/steam stripping tower containing suitable trays or packing material to desorb the absorbed acid gases. Details concerning the apparatus in regeneration zone 200 are known to those skilled in the art. Regeneration zone 200 is typically operated at a temperature of about 100° to 130°C and a pressure of about 15 to 50 psia. A portion of the vapors emerging from the top of the regeneration zone 200 may optionally be condensed and returned to the process. All remaining vapors are discharged from the regeneration zone via line 16.

A regenerated absorbent composition stream, which is depleted in acid gases relative to the acid gas-rich absorbent composition stream, is withdrawn from regeneration zone 200. A portion of the regenerated absorbent composition stream is commonly passed to a reboiler and reintroduced to regeneration zone 200. The remainder of the regenerated absorbent composition stream is recycled to absorption zone 100 via lines 17, 18 and 11.

The regenerated absorbent composition is commonly cooled before being reused in absorption zone 100. Cooling of the regenerated absorbent composition can be accomplished with standard equipment known to those skilled in the art. For example, in the Figure heat is exchanged between absorbent composition streams using a lean rich exchanger in cooling zone 400 and heat is removed from the system using a conventional heat exchanger in cooling zone 500.

BEST AVAILABLE COPY

The process illustrated in the Figure is provided as an example. Workers in the art have devised many process variations to optimize the performance of a particular absorbent composition or to minimize capital or operating costs associated with acid gas removal from a particular sour gas stream. These variations include multiple absorption zones or increased reliance on flash zones for rich absorbent regeneration (up to and including elimination of the stripping zone).

The relatively high level of piperazine in the absorbent composition results in a number of improvements in absorption performance. Most notably, an equivalent amount of CO₂ can be removed from an acid gas-rich gas stream at a lower absorbent composition circulation rate using the present absorbent composition. Equivalent CO₂ removal at lower absorbent composition circulation rates reduces the size and capital cost of vessels, heat exchangers, pumps, and associated piping. Lower absorbent composition circulation rates also eliminate operating costs associated with pumping, heating and cooling the extra liquid.

Alternatively, the amount of CO₂ removed from a gas stream contacted with the absorbent composition is increased at a given absorbent composition circulation rate. Hence, the capacity and profitability of existing equipment can be measurably improved using the present absorbent composition.

Moreover, the present absorbent composition allows for operation at higher absorber temperatures, which is advantageous because high liquid phase temperatures typically reduce or limit absorption. Hence, an absorbent composition which provides equivalent acid gas removal at higher liquid phase temperatures is

superior to an absorbent composition which requires lower liquid phase temperatures. While not wishing to be bound by theory, it is likely there is a close relationship between the minimum absorbent composition circulation rate required to adequately clean a particular gas and the liquid phase temperature profile in the absorber. It is well known that absorption of CO₂ into aqueous amine solutions liberates heat of absorption into the circulating absorbent composition. Hence, as the circulation rate decreases, liquid phase absorber temperatures increase for a fixed degree of CO₂ removal.

The absorbent composition also provides for further advantages downstream in the acid gas removal process. For example, certain downstream equipment such as flash tanks and lean/rich exchangers commonly found in gas treating facilities typically operate better as the rich amine temperature increases. An acid gas-rich absorbent composition leaving the absorber at a higher temperature therefore provides operational benefits to the downstream equipment.

In addition to CO₂, the absorbent composition has absorption capacity for H₂S, COS and mercaptans. Accordingly, preferably the product gas stream removed via line 12 is also at least partially depleted in these acid gases relative to the feed gas stream. As is known in the art, the degree of removal of these other acid gases can be controlled by adjusting the equipment and conditions in the absorption process.

The following examples further illustrate the invention.

Example 1

A gas stream containing CO₂ was treated in a pilot scale absorber to remove the CO₂. The absorber was a 10 ft. high, 2 inch

BEST AVAILABLE COPY

inside diameter column packed with $\frac{1}{4}$ inch ceramic saddles. Lean absorbent was introduced at the top of the absorber and sour gas was introduced at the bottom. The two streams were contacted counter currently. The CO₂ rich absorbent left the absorber at the bottom. The sweet gas exited the absorber at the top.

The CO₂ rich absorbent was regenerated in an 8.5 ft high, 2 inch inside diameter stripper column packed with $\frac{1}{4}$ inch Protruded Pro-Pack packing. The stripper was equipped with a reboiler at the bottom and an overhead condenser at the top. Reflux water collected in the stripper overhead was returned to the circulating solution.

The above described pilot scale equipment, together with associated instruments for measurement of temperature, pressure, gas flow rate, liquid flow rate, gas phase composition, liquid phase composition etc. were used to measure the effect of piperazine concentration on the minimum circulation rate required to achieve a given degree of CO₂ removal. The minimum absorbent circulation required to achieve a given amount of CO₂ removal was determined by gradually decreasing circulation until the working capacity of the solvent was exhausted. At this point, an incremental reduction in circulation results in a rapid increase in the sweet gas concentration of CO₂. However, restoring the missing circulation increment returns the sweet gas concentration to normal (less than 50 ppmv in this case).

This procedure provides a direct measurement of the working capacity of a particular absorbent composition in a typical absorber-stripper cycle. Other methods, such as those based on vapor liquid equilibrium measurements, require experience or simulation based corrections to account for the effects of typical process constraints such as elevated absorber temperatures, limited gas-liquid contact time, imperfect absorbent stripping etc.

The data in Table 1 demonstrate absorbent compositions containing more than 1.0 mole/liter piperazine provide equivalent CO₂ removal at a lower liquid circulation rate. Furthermore, equivalent CO₂ removal was achieved despite the higher absorption zone temperatures and the higher rich absorbent temperature. Surprisingly, these results were achieved, in this case, without a measurable increase in the heat requirement to strip CO₂ from the rich absorbent.

Table 1

	0.95 M piperazine	1.5 M piperazine
Sweet CO ₂ Concentration (ppmv)	< 50	< 50
Minimum Circulation Rate (g/min)	230	210
Bed Position 3 T (F)	180	200
Bed Position 4 T (F)	188	201
Bed Position 5 T (F)	190	201
Rich T (F)	183	189
Reboiler Duty (BTU/hr)	4,550	4,530

Example 2

The pilot scale equipment described in Example 1 can also be used to measure the effect of piperazine concentration on the volume of gas which can be conditioned by a given set of equipment with a fixed flow rate of liquid absorbent. In this case the absorbent circulation rate is held constant and the sour gas flow rate is increased until the liquid absorbent capacity is exhausted and the sweet gas concentration of CO₂ rises above a predetermined value (50 ppmv in this case).

The data in Table 2 demonstrate absorbent compositions containing more than 1.0 mole/liter piperazine allow the same equipment circulating the same amount of liquid absorbent to process more sour gas to a given specification.

Table 2

	0.95 M piperazine	1.5 M piperazine
Sweet CO ₂ Concentration (ppmv)	< 50	< 50
Maximum Gas Throughput (SLPM)	92.1	98.1
Bed Position 3 T (F)	180	165
Bed Position 4 T (F)	188	190
Bed Position 5 T (F)	190	198
Rich T (F)	183	191
Reboiler Duty (BTU/hr)	4,550	4,686

We claim:

1. An absorbent composition for the removal of acid gases from gas streams, comprising an aqueous solution comprising: 1) greater than 1 mole piperazine per liter of aqueous solution; and 2) about 1.5 to about 6 moles methyldiethanolamine per liter of aqueous solution.

2. The absorbent composition of claim 1, comprising greater than about 1.1 mole piperazine per liter of aqueous solution.

3. The absorbent composition of claim 1, comprising greater than about 1.2 mole piperazine per liter of aqueous solution.

4. The absorbent composition of claim 1, comprising about 2.5 to about 5.5 mole methyldiethanolamine per liter of aqueous solution.

5. The absorbent composition of claim 1, comprising about 2.9 to about 4.2 mole methyldiethanolamine per liter of aqueous solution.

6. The absorbent composition of claim 1, further comprising an additional chemical solvent or a physical solvent.

7. The absorbent composition of claim 6, comprising a physical solvent selected from the group consisting of sulfolane or methoxytriglycol.

BEST AVAILABLE COPY

8. A process for the removal of acid gases from a gas stream, comprising contacting a gas stream containing an acid gas with an absorbent composition comprising an aqueous solution comprising: 1) greater than 1 mole piperazine per liter of aqueous solution; and 2) about 1.5 to about 6 moles methyldiethanolamine per liter of aqueous solution to produce an acid gas-lean gas stream and an acid gas-rich absorbent composition stream.

9. The process of claim 8, further comprising the subsequent steps of separating the acid gas-lean gas stream from the acid gas-rich absorbent composition stream; recovering the acid gas-lean gas stream as product; regenerating the acid gas-rich absorbent composition stream by removing acid gas therefrom to produce a regenerated absorbent composition; and recycling the regenerated absorbent composition to the contacting step of claim 8.

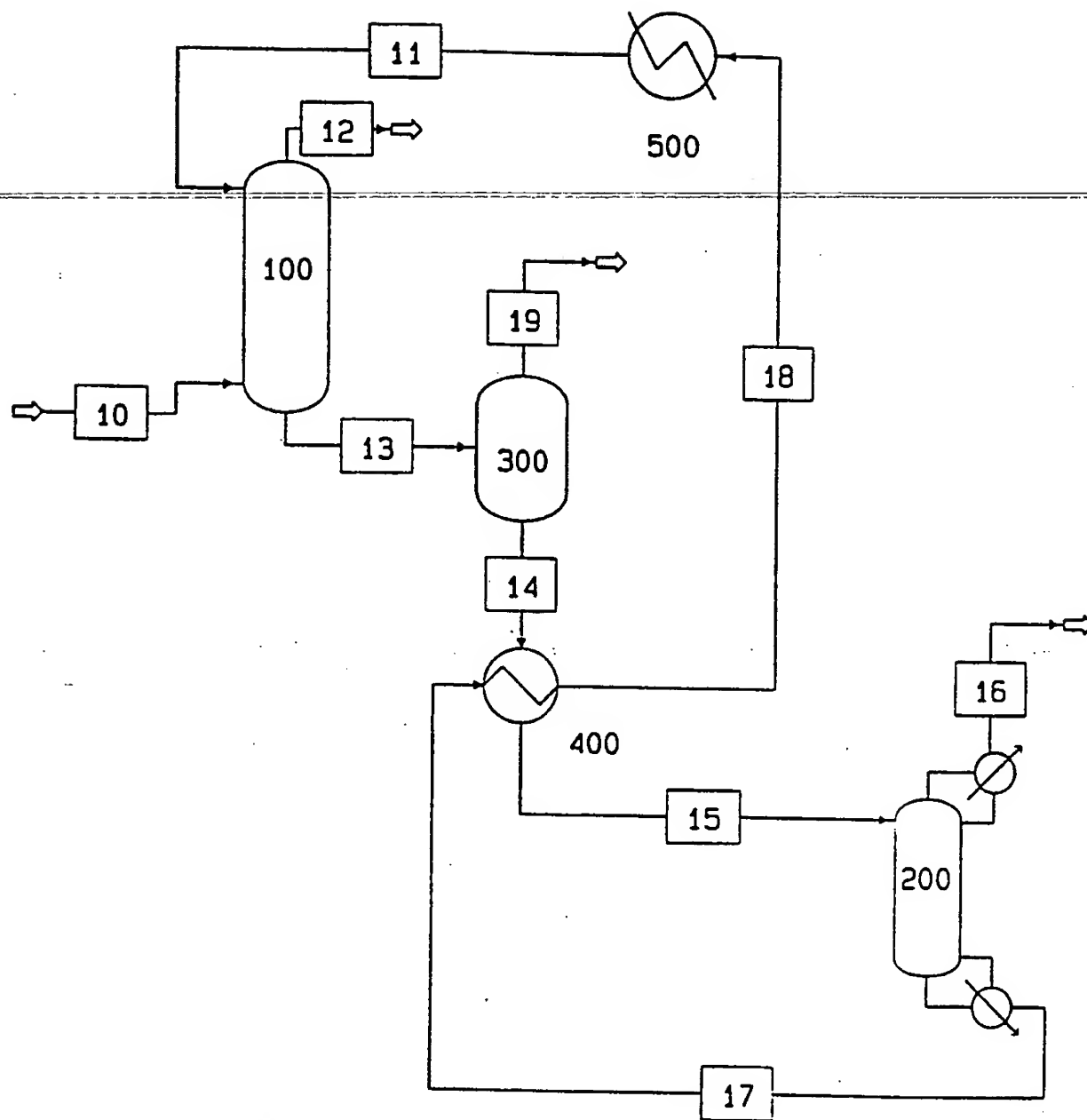
10. The process of claim 8, wherein the absorbent composition comprises greater than about 1.1 mole piperazine per liter of aqueous solution.

11. The process of claim 8, wherein the absorbent composition comprises about 2.5 to about 5.5 mole methyldiethanolamine per liter of aqueous solution.

12. The process of claim 8, wherein the absorbent composition further comprises an additional chemical solvent or a physical solvent.

13. The process of claim 8, wherein the regenerating step is conducted at a temperature in the range of about 100° to about 130°C.

BEST AVAILABLE COPY



BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

Inte ic Application No
PCT/US 00/11635

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 336 233 A (APPL MAX ET AL) 22 June 1982 (1982-06-22) cited in the application column 3, line 8 - line 24; claims 1-9	1-13
A	EP 0 705 637 A (KANSAI ELECTRIC POWER CO ;MITSUBISHI HEAVY IND LTD (JP)) 10 April 1996 (1996-04-10) page 3, line 27 -page 4, line 1	1-13
A	US 5 209 914 A (LE COZ PHILIPPE ET AL) 11 May 1993 (1993-05-11) column 1, line 5 - line 10 column 1, line 57 -column 4, line 27; claims 1,5-9	1-13
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 August 2000

Date of mailing of the international search report

16/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/11635

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 224 348 A (ICI PLC) 3 June 1987 (1987-06-03) the whole document	1-13

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

Information Patent family members

Index Application No

PCT/US 90/11635

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4336233 A	22-06-1982	DE 2551717 A	02-06-1977
		AT 365942 B	25-02-1982
		AT 854176 A	15-07-1981
		BE 848483 A	18-05-1977
		CA 1090098 A	25-11-1980
		CS 219323 B	25-03-1983
		ES 453391 A	16-03-1978
		FR 2332049 A	17-06-1977
		GB 1560905 A	13-02-1980
		JP 1355979 C	24-12-1986
		JP 52063171 A	25-05-1977
		JP 61019286 B	16-05-1986
		NL 7612855 A, B,	23-05-1977
EP 0705637 A	10-04-1996	JP 8103630 A	23-04-1996
		JP 8252430 A	01-10-1996
		JP 8257354 A	08-10-1996
		JP 8257355 A	08-10-1996
		CN 1127156 A	24-07-1996
		EP 0880990 A	02-12-1998
		EP 0879631 A	25-11-1998
		EP 0880991 A	02-12-1998
		NO 953103 A	09-04-1996
		US 5618506 A	08-04-1997
US 5209914 A	11-05-1993	FR 2631852 A	01-12-1989
		FR 2631853 A	01-12-1989
		FR 2640157 A	15-06-1990
		AT 103201 T	15-04-1994
		DE 68914040 D	28-04-1994
		DE 68914040 T	13-10-1994
		EP 0348251 A	27-12-1989
		ES 2054049 T	01-08-1994
		WO 8911327 A	30-11-1989
		JP 2504367 T	13-12-1990
		JP 2925619 B	28-07-1999
		RU 2040956 C	09-08-1995
		US 5348714 A	20-09-1994
		US 5277885 A	11-01-1994
		DD 283777 A	24-10-1990
EP 0224348 A	03-06-1987	NO 864574 A, B,	19-05-1987

BEST AVAILABLE COPY